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(56) Documents Cited

EP 0559101 A

EP 0545452 A

EP 0540295 A

EP 0427892 A

EP 0363104 A

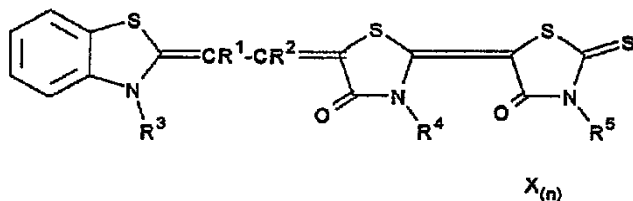
(58) Field of Search

UK CL (Edition M) G2C CC19K7

INT CL⁶ G03C

(54) **Sensitised photographic silver halide materials**

(57) A method of improving the raw stock stability of a photographic material comprising a support bearing a silver halide emulsion layer sensitised to radiation having a wavelength of from 600 to 690 nm characterised in that the sensitising dye is a tricyclic merocyanine of the general formula:



wherein R^1 , and R^2 are each hydrogen or a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and

R^3 , R^4 and R^5 are each a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and wherein at least two of R^3 , R^4 and R^5 contain a water-solubilising group, e.g. -OH, -COOH, -SO₃H.

X is a counter-ion, and
n is 0-3.

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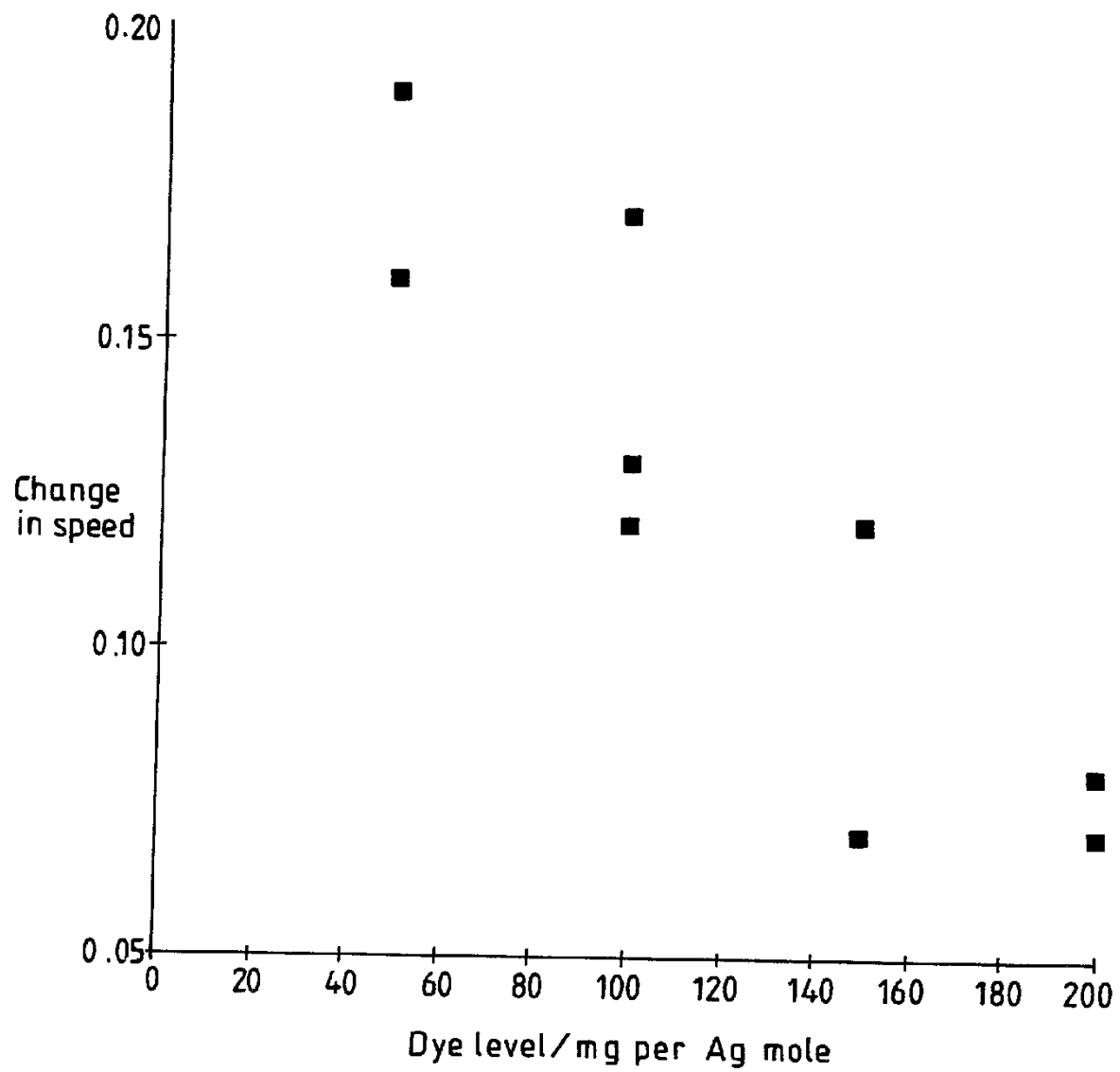


Fig.1.

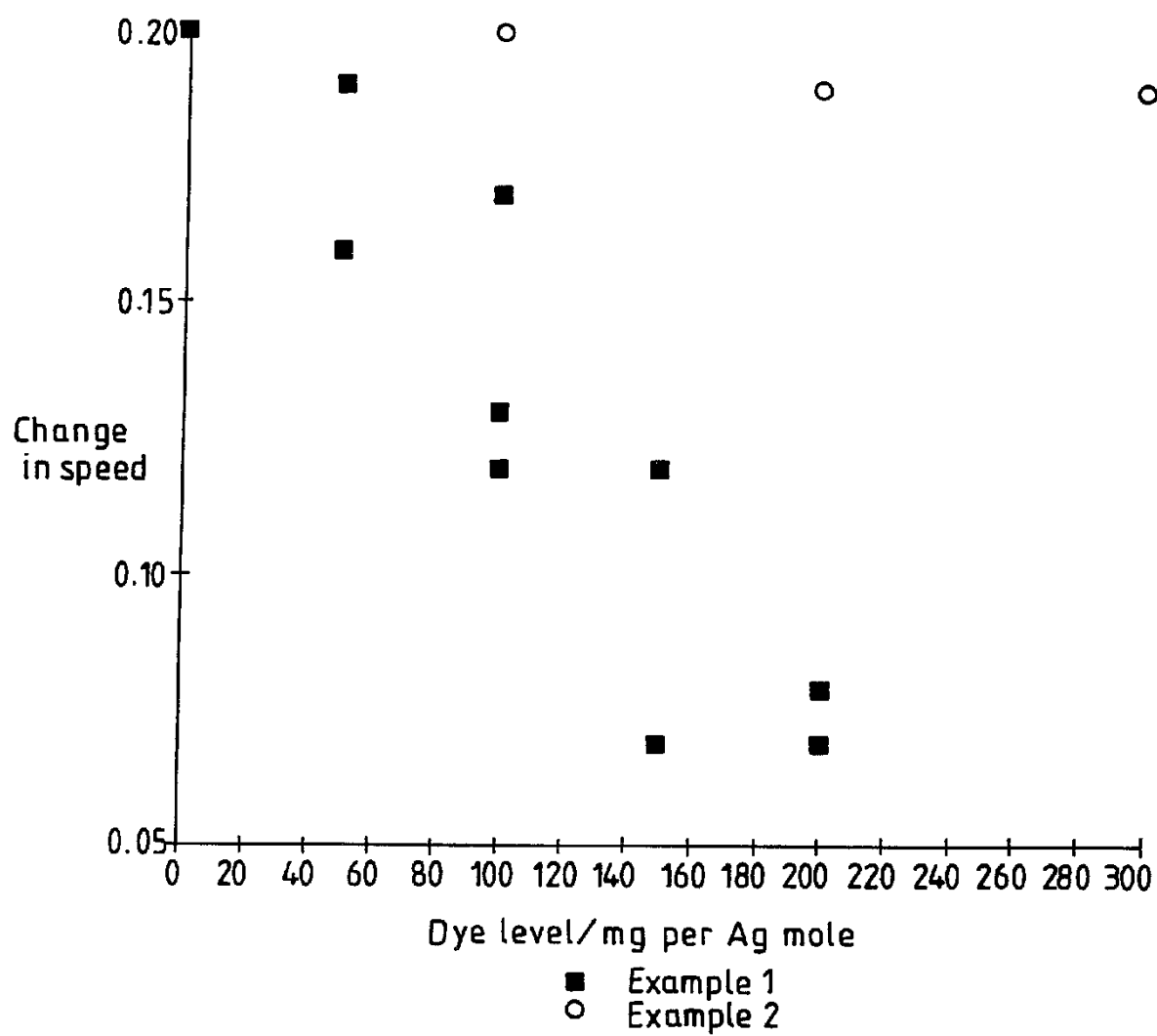


Fig.2.

**PHOTOGRAPHIC SILVER HALIDE MATERIALS HAVING IMPROVED
RAW STOCK STABILITY**

Cross-reference to Related Applications

Co-filed British applications (ref 8595)

5 Field of the Invention

The present invention relates to photographic silver halide materials having improved raw stock stability (shelf life), particularly to materials intended for exposure to radiation having a wavelength
10 of from 600-690 nm, eg radiation from a Helium-Neon laser or laser diode exposing source, and especially to materials intended for exposure in graphic arts equipment.

Background of the Invention

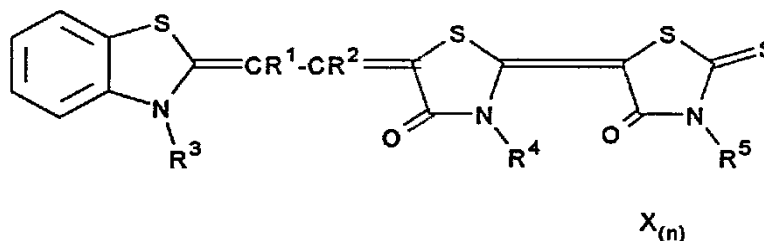
15 Classes of sensitising dyes have previously been proposed for preparing silver halide materials that are both sensitive to red radiation having a wavelength of from 600-690 nm. For example, British Patent Specification 1 471 701 and European
20 Specification 0 363 104 describe the use of tri-heterocyclic dyes for this purpose.

Problem to be Solved by the Invention

A problem with such materials is that they do not have the desired raw stock stability (shelf life).

25 Summary of the Invention

According to the present invention, therefore, there is provided a method of improving the raw stock stability of a photographic material comprising a support bearing a silver halide emulsion layer
30 sensitised to radiation having a wavelength of from 600 to 690 nm characterised in that the sensitising dye is a tricyclic merocyanine of the general formula:



wherein R^1 , and R^2 are each hydrogen or a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and

5 R^3 , R^4 and R^5 are each a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and wherein at least two of R^3 , R^4 and R^5 contain a water-solubilising group,

X is a counter-ion, and

10 n is 0-3.

Advantageous Effect of the Invention

The sensitising dyes defined above not only sensitise the emulsion to light of 600-690 nm, for example, as emitted by a Helium-Neon laser or laser
15 diode radiation source, but also provide improved raw stock keeping properties.

Brief Description of the Drawings

Fig 1 of the accompanying drawings illustrates the results of Example 1 below.

20 Detailed Description of the Invention

The water-solubilising groups on R^3 to R^5 may be hydroxyl or acid groups, for example -OH, -COOH or -SO₃H groups. Preferably both of groups R^4 and R^5 contain a water-solubilising group.

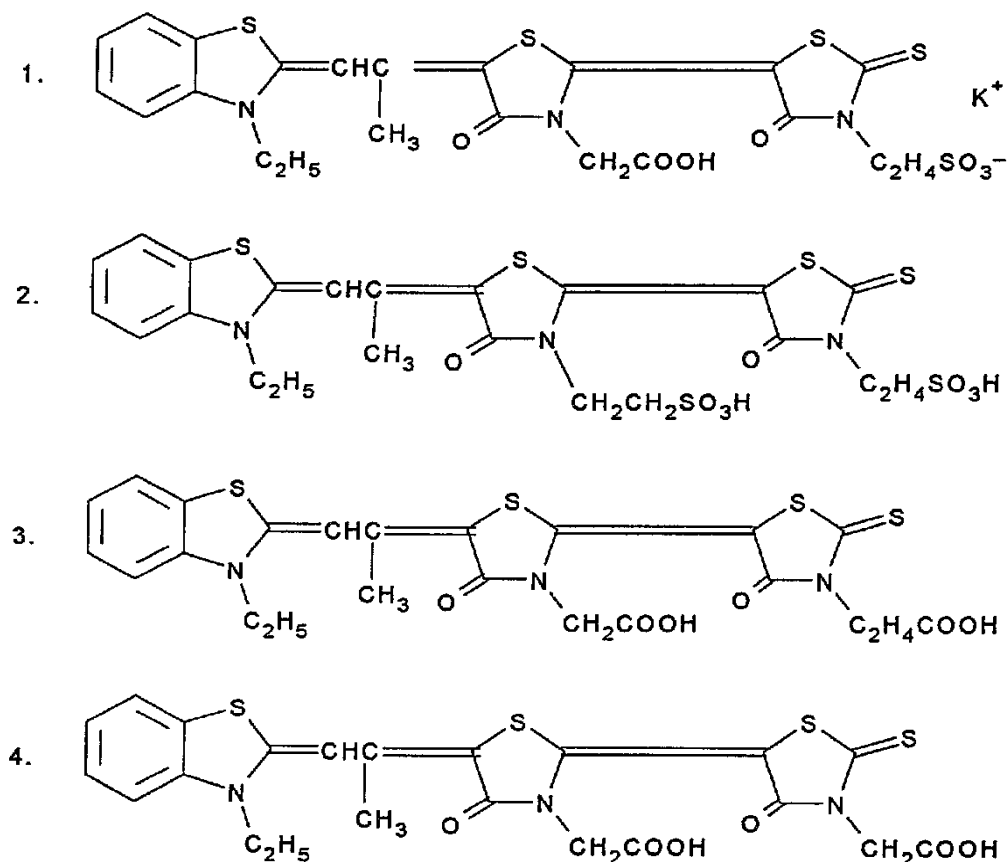
25 Examples of alkyl groups which R^1 to R^5 may represent are methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, n-pentyl or t-pentyl. The alkyl groups may be substituted with halogen atoms, alkyl, substituted alkyl, aryl or substituted aryl groups.

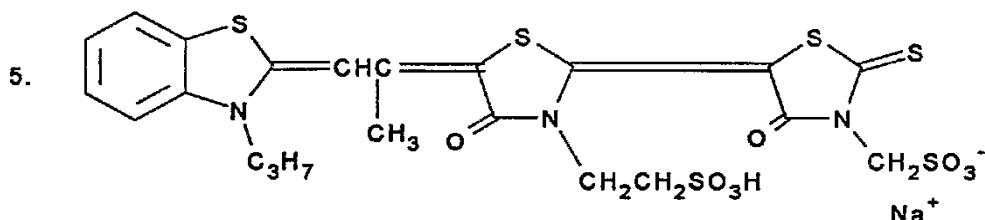
The counter-ion X is preferably ammonium or an alkali metal, eg. Na^+ , although the dyes may exist in the free acid form ($n=0$).

5 The dyes may be prepared by known methods, for example the dyes may be prepared by those methods described in "Cyanine Dyes and Related Compounds", by F M Hamer, Interscience, 1964. They may be incorporated into the silver halide emulsion as a solution in water or an alcohol in known manner.

10 Examples of dyes to be used in the present invention are listed in Table 1:

TABLE 1





The dye may be present in the present materials in amounts of from 5 to 500, preferably from 50 to 250, more particularly from 100 to 200 mg per mole of silver halide in the emulsion layer.

The silver halide emulsion is preferably of the type that provides a high contrast image as required in graphic arts applications. Such emulsions are customarily high in silver chloride and low in silver iodide. They may be silver halide emulsions which contain both silver bromide and silver iodide in addition to the silver chloride. Preferably the iodide content is less than 10 mole percent. Substantially pure silver chloride emulsions may be used although the preferred emulsions comprise 70 mole % chloride and 30 mole % bromide. As is known in the graphic arts field the grains may be doped with Rhodium, Ruthenium, Iridium or other Group VIII metals. The emulsions may be negative or direct positive emulsions, mono- or poly-disperse.

Preferably the silver halide grains are doped with Group VIII metal at levels in the range 10^{-9} to 10^{-3} , preferably 10^{-6} to 10^{-3} , mole metal per mole of silver. The preferred Group VIII metal is Rhodium.

The emulsions employed and the addenda added thereto, the binders, supports, etc may be as described in Research Disclosure Item 308119, December 1989 published by Kenneth Mason Publications, Emsworth, Hants, United Kingdom.

The light-sensitive silver halide contained in the photographic elements can be processed following exposure to form a visible image by associating the silver halide with an aqueous alkaline medium in the presence of a developing agent contained in the medium or the element. It is a distinct advantage of the present invention that the described photographic elements can be processed in conventional developers as opposed to specialised developers conventionally employed in conjunction with lithographic photographic elements to obtain very high contrast images. When the photographic elements contain incorporated developing agents, the elements can be processed in the presence of an activator, which can be identical to the developer in composition, but otherwise lacking a developing agent.

Very high contrast images can be obtained at pH values in the range of from 11 to 12.3, but preferably lower pH values, for example below 11 and most preferably in the range of 10.3 to 10.5 are preferably employed for processing the photographic recording materials as described herein.

The developers are typically aqueous solutions, although organic solvents, such as diethylene glycol, can also be included to facilitate the solvency of organic components. The developers contain one or a combination of conventional developing agents, such as a polyhydroxybenzene, aminophenol, para-phenylenediamine, ascorbic acid, pyrazolidone, pyrazolone, pyrimidine, dithionite, hydroxylamine or other conventional developing agents.

It is preferred to employ hydroquinone and 3-pyrazolidone developing agents in combination. The pH of the developers can be adjusted with alkali metal hydroxides and carbonates, borax and other basic

salts. To reduce gelatin swelling during development, compounds such as sodium sulphate can be incorporated into the developer. Also, compounds such as sodium thiocyanate can be present to reduce granularity.

5 Chelating and sequestering agents, such as ethylene-diaminetetraacetic acid or its sodium salt, can be present. Generally, any conventional developer composition can be employed in the practice of this invention. Specific illustrative photographic
10 developers are disclosed in the Handbook of Chemistry and Physics, 36th Edition, under the title "Photographic Formulae" at page 3001 et seq. and in Processing Chemicals and Formulas, 6th Edition, published by Eastman Kodak Company (1963). The
15 photographic elements can, of course, be processed with conventional developers for lithographic photographic elements, as illustrated by US Patent No. 3,573,914 and UK Patent No. 376,600.

The support may be any photographic support, for
20 example, transparent film or reflective paper support, eg. polyethylene coated paper.

For paper materials, it is customary to employ a fluorescent brightening agent. These may be incorporated into the materials by known techniques,
25 for example by dissolving a water-soluble brightener in the gelatin supercoat (the layer most remote from the support). In one embodiment a water-insoluble brightener may be used. It may be imbibed onto particles of a polymer dispersion as described in
30 British Patent Specification 1,504,949 or 1,504,950 or dissolved in droplets of coupler solvents prior to incorporation in a layer of the material, e.g. in the supercoat.

In general the present photographic materials may
35 contain silver halide emulsions, additives, additional

layers, etc, as described in Research Disclosure, December 1978, Item 17643, published by Industrial Opportunities Ltd, 'The Old Harbourmaster', 8 North Street, Elmsworth, Hants PO10 7DD, UK.

- 5 The following Example is included for a better understanding of the invention.

EXAMPLE 1

10 In this example, the merocyanine dye (4) of Table 1 above was added at the rate of 0, 50, 100, 150 or 200 mg per silver mole to an emulsion which had been previously chemically sensitised. The emulsion, a monodispersed 70:30 Cl:Br cubic emulsion, was typical of the kind often used for Graphic Arts or Colour Paper product applications. In all, ten experiments
15 were made such that the following dye level variations were obtained:

	Experiment	Dye level
20	1	0 mg per Ag mole
	2 and 3	50 mg per Ag mole
	4, 5 and 6	100 mg per Ag mole
	7 and 8	150 mg per Ag mole
	9 and 10	200 mg per Ag mole

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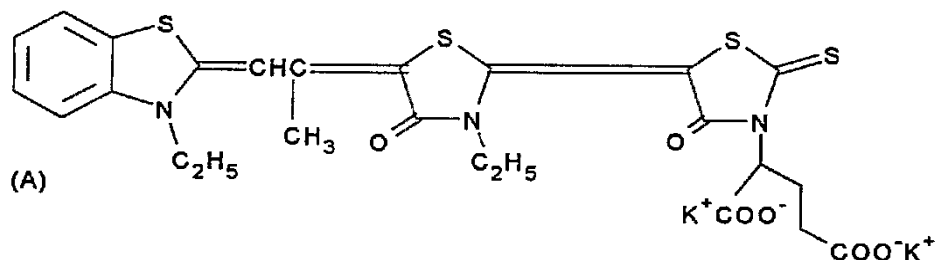
After coating the emulsion samples on a polyethylene terephthalate support, the resulting coatings were sealed in foil bags and kept for 7 days in ambient humidity conditions at 49°C. This was a
30 typical procedure used to test emulsion raw stock keeping (RSK) stability. At the end of 7 days, the coatings were exposed for 10^{-6} seconds using a tungsten bulb and a Wratten 29 (red) filter, together with a 0-2 logE/0.1 increment step wedge. Another set
35 of the same coatings, that had not been subjected to

the elevated temperature conditions but were instead stored at ambient humidity at 21°C, were exposed at the same time and in the same way to serve as control samples. The two sets of exposed coatings were
5 processed for 30 seconds in Kodak® RA2000 developer in an Interpro RA20 processor and the densities so produced measured and plotted.

Several parameters were derived from the densitometry results and in particular the speed of
10 the coatings was measured at a density of (Dmin + 0.6). The difference in speed between the coatings kept for 7 days at 49°C (the experiment) and the coatings stored at 21°C (the control) are plotted in figure 2 as a function of dye level. It was clear
15 from these results that as the level of this sensitising dye was increased the change in speed due to keeping instability was consistently reduced. It should be noted that the level of dye needed to completely stabilise an emulsion would be dependent on
20 the size and type of emulsion used and could be determined by normal experiment.

EXAMPLE 2 (Comparative)

Example 1 was repeated using a dye A of the formula:

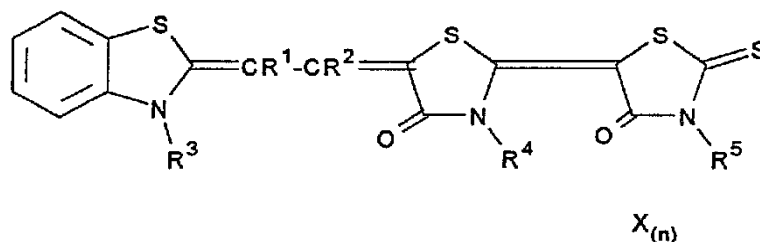


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Fig 2 shows the results of both Example 1 and Example 2 plotted on the same axes to clearly show that Dye A does not show the stabilising effect of the dyes of the invention.

CLAIMS:

1. A method of improving the raw stock stability of a method comprising a support bearing a silver halide emulsion layer sensitised to radiation having a wavelength of from 600 to 690 nm characterised in that the sensitising dye is a tricyclic merocyanine of the general formula:



- wherein R^1 , and R^2 are each hydrogen or a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and

- R^3 , R^4 and R^5 are each a substituted or unsubstituted alkyl group of 1-5 carbon atoms, and wherein at least two of R^3 , R^4 and R^5 contain a water-solubilising group,

X is a counter-ion, and
 n is 0-3.

2. A method as claimed in claim 1 in which the silver halide emulsion is a high contrast silver chlorobromide emulsion comprising at least 50 mole % silver chloride.

3. A method as claimed claim 1 or 2 in which the silver halide emulsion comprises at least 70% chloride and less than 10% iodide.

4. A method as claimed in any of claims 1-3 in which both R^4 and R^5 of the formula of claim 1 contain a water-solubilising group.

5. A method as claimed in any of claims 1 to 4 in which the silver halide emulsion is doped with

Rhodium, Ruthenium, Osmium, Iridium or other Group VIII metals.

6. A method as claimed in claim 5 in which the Group VIII metal dopant is present in amounts in the range 10^{-9} to 10^{-3} , preferably 10^{-6} to 10^{-3} , mole Group VIII metal per mole of silver.

7. A photographic material prepared by the method of any of claims 1-6.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
GB 9319791.1

Relevant Technical Fields

(i) UK Cl (Ed.M) G2C - CC19 K7

(ii) Int Cl (Ed.5) G03C

Search Examiner
M K B REYNOLDS

Date of completion of Search
24 OCTOBER 1994

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii)

Documents considered relevant following a search in respect of Claims :-
1-7

Categories of documents

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|---|---|
| X: Document indicating lack of novelty or of inventive step. | P: Document published on or after the declared priority date but before the filing date of the present application. |
| Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. | E: Patent document published on or after, but with priority date earlier than, the filing date of the present application. |
| A: Document indicating technological background and/or state of the art. | &: Member of the same patent family; corresponding document. |

Category	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0545452 A (AGFA) pages 10-12	1, 4-6
X	EP 0540295 A (KONICA) pages 3-9, 11, Examples	1-4
X	EP 0559101 A (CANON) pages 4-5, compounds c-1, c-7	1
X	EP 0427892 A (AGFA) pages 5-11, Examples	1-4
X	EP 0363104 A (KODAK) page 2	1

Databases:The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).